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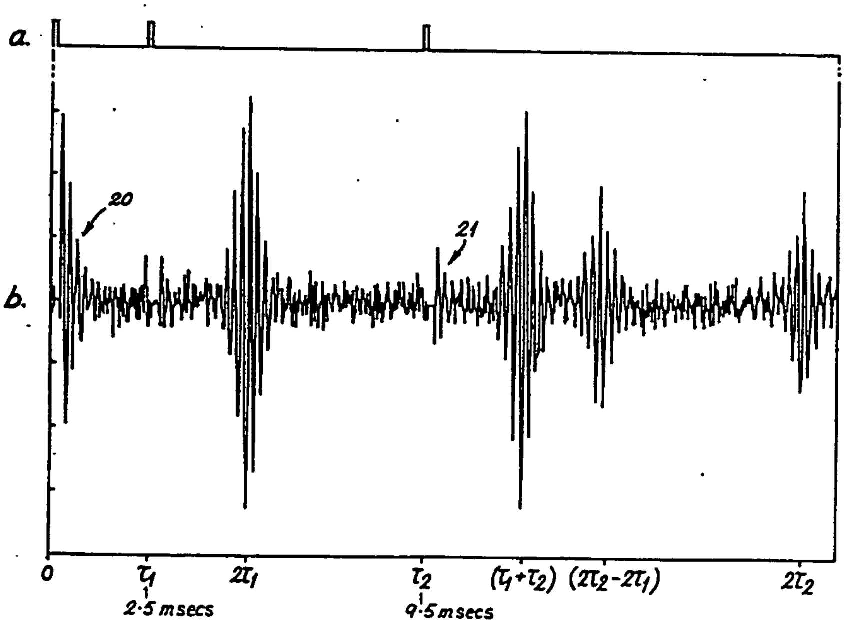

(57) Abstract

A method of Nuclear Quadrupole Resonance testing includes the steps of applying to a sample in which selected nuclei have an integral spin quantum number a series of at least three pulses of electromagnetic waves at a single radiofrequency to excite quadrupole resonance of the selected nuclei (waveform (a)), and detecting responses at a plurality of times when echo response signals are expected to occur (waveform (b)).

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IMPROVEMENTS IN NQR TESTING

The present invention relates to a method of nuclear quadrupole resonance (NQR) testing of integral spin quantum number spin systems.

NQR testing is used for detecting the presence or disposition of specific substances. It depends on the energy levels of quadrupolar nuclei, which have a spin quantum number greater than one-half. Quadrupolar nuclei having an integral spin quantum number (that is, I = 1, 2, 3 ...) include ^{14}N (I=1). ^{14}N nuclei are present in a wide range of substances, including animal tissue, bone, food-stuffs, explosives and drugs.

In the sub-molecular environment of compounds or crystals, the nature and disposition of the electrons and atomic nuclei produce an electric field gradient which modifies the nuclear energy levels to such an extent that measurements of NQR effects can indicate not merely the nuclei which are present but also their chemical environment, thus indicating specific substances or types of substances in any tested sample.

In NQR testing a sample is irradiated with pulses or sequences of pulses of radiofrequency electromagnetic waves having a frequency which is at or very close to a resonant frequency of quadrupolar nuclei in a substance which is to be detected. If the substance is present, the irradiant energy will raise at least some of the nuclei to a higher energy level. Such nuclei will tend to return to their normal state and in doing so they will emit radiation at their resonance frequency or frequencies which can be detected as a free induction decay (f.i.d.) during a decay period after each pulse. These emissions decay at a rate which depends on two relaxation time constants, T_1 and T_2.

In conventional NQR testing, either a substantial part of the free induction decay is measured after each pulse or the responses are measured as echoes in relatively short sampling periods between or following a relatively rapid succession of

pulses. Usually the results from a number of test pulses or test sequences are integrated to improve the signal-to-noise ratio. Various schemes of pulse sequences have been used.

In a scientific paper by Grechiskin et al. (Adv. N.Q.R., 1983, 5, 1) it has been predicted theoretically that conditions might arise which could give rise to the formation of a single echo as well as a free induction decay from nuclei of unity spin quantum number when excited by two excitation pulses at a single radiofrequency. No details are given as to how, or even whether, this can be achieved experimentally.

In a paper by Bloom et al. (Physical Review 1955, vol. 97, 1699) it has been reported that multiple echoes as well as a free induction decay have been observed in tests from nuclei of spin quantum number 3/2 in a weak magnetic field. The paper demonstrates that the magnetic field removes degeneracies which would otherwise so broaden and attenuate the echoes that no useful NQR information would be yielded. However, this technique would not be expected to work for integral spin systems, since such systems are not strongly affected by a weak applied magnetic field.

According to the present invention, a method of NQR testing includes the steps of applying to a sample in which selected nuclei have an integral spin quantum number a series of at least three pulses of electromagnetic waves at a single radiofrequency to excite quadrupole resonance of the selected nuclei and detecting responses at a plurality of times when echo response signals are expected to occur.

We have found that, surprisingly, for samples in which the selected nuclei have an integral (e.g. unity) spin quantum number, in addition to the free induction decay which occurs immediately after a single frequency excitation pulse, there are some substantial NQR echo responses which occur after delays matching the time intervals between preceding pulses. It has been found that, if time τ is measured from the first pulse of a series of pulses of pre-selected widths and phases occurring at

times 0, τ_1, τ_2 .... τ_N which are not necessarily identically spaced there are substantial echo responses at many, although not all of, the following times:

$$\tau_n + \tau_n = 2\tau_n$$
$$\tau_n + (\tau_n - \tau_1) = 2\tau_n - \tau_1$$
$$\dots\dots\dots\dots\dots\dots\dots\dots$$
$$\tau_n + (\tau_n - \tau_{n-1}) = 2\tau_n - \tau_{n-1}$$

where n = 1 to N. It has also been found that there can be echo responses which occur after a delay which matches the time interval between an excitation pulse and a echo response which precedes it, for instance at times

$$\tau_n + (\tau_n - 2\tau_1) = 2\tau_n - 2\tau_1.$$

The times when echo response signals would be expected to occur for a particular substance or class of substance can be predetermined by experimentation in a manner which will be evident to a person skilled in the art.

It will be appreciated that, since more (often many more) echoes may be detected from the sample than excitation pulses are applied to the sample, and since the usual f.i.d.'s may also be detected, a larger signal-to-noise ratio can be obtained than would be obtained for a system in which a multiple echo train was not generated; the sensitivity of the tests can thus be improved. Therefore, it is preferred that the responses to the excitation pulses are summed.

For simplicity and economy, it is preferred that the application and detection steps take place in the absence of an applied magnetic field.

Preferably, the interval between the first and second pulses of the series is different from the interval between the second and third pulses. It has now been discovered that, using such intervals, stimulated NQR echoes can be generated, with the attendant possibility of there being more echoes generated and detected than there are pulses applied. This can in turn afford the advantage of larger signal-to-noise ratio and increased sensitivity mentioned previously.

The pulse times τ_n are preferably chosen to have no common factor and so that the echo times are distinct and separated from the excitation pulse times. Preferably $\tau_n > 2\tau_{n-1}$ and in some cases it may be necessary to have the condition $2\tau_N < T_1$ where T_1 is the spin-lattice relaxation time for the resonance being tested. The time intervals $(\tau_n - \tau_{n-1})$ may be greater than those used in conventional NQR test pulse sequences; usually $(\tau_n - \tau_{n-1}) > T_2^*$, where T_2^* is the f.i.d. time.

In a preferred embodiment, the pulses of the series are applied at times 0, τ_1 and τ_2 and the echo response signals are measured in periods embracing at least some of the times $2\tau_1$, $\tau_1 + \tau_2$, $2\tau_2$ and $2\tau_2 - 2\tau_1$. It is also preferred that $\tau_2 > 2\tau_1$ and τ_1 and τ_2 have values which make the times τ_1, τ_2, $2\tau_1$, $\tau_1 + \tau_2$, $2\tau_2 - 2\tau_1$ and $2\tau_2$ separate and distinct from one another.

If pulses are applied to the sample at times 0, τ_1 and τ_2, it has been found that there may be little or no substantial echo response at time $2\tau_2 - \tau_1$ for integral spin quantum number systems. This fact can be used effectively to perpetuate or at least prolong the echo train. A further excitation pulse may be applied at time $2\tau_2 - \tau_1$. This will produce further echoes without suppressing or affecting the quality of detectable NQR information. Additional pulses may be applied at some or all of times $(2\tau_n - \tau_{n-1})$ (n = 3, 4, 5 .....) to further prolong the multiple echo train. There may be times other than $(2\tau_n - \tau_{n-1})$ when there are no substantial echo responses. In this case, the further excitation pulses could be applied at these times additionally or instead.

Preferred features of the invention will now be described with reference to the accompanying drawings, in which:-

Figure 1 is a block circuit diagram of apparatus for NQR testing; and

Figure 2 is a graphical diagram showing response signals detected in a test with the apparatus of Figure 1.

In Figure 1 a radiofrequency source 10 is connected to an rf power amplifier 11. The output of rf amplifier 11 is connected

through switching and timing circuits 12 to r.f. coils 13 which are disposed about the sample to be tested (not shown). The switching and timing circuits 12 also connect the coils 13 to a detecting and measuring circuit 14, which is also connected to a graphical recorder 15. The switching and timing circuits 12 also control the timing and phase of the signals applied by the r.f. source 10 to the r.f. power amplifier 11. It will be appreciated that numerous modifications to the apparatus described are possible, as will be apparent to the skilled person.

In Figure 2 waveform (a) represents the excitation pulse control signals applied to control a series of three single frequency excitation pulses, and waveform (b) represents the graphical recorder trace of detected NQR responses. A time scale is shown below this trace. As shown, the excitation pulses occurred at times $\tau = 0$, 2.5 ms (τ_1) and 9.5 ms (τ_2). The pulse sequence was of the form $90°_0-\tau_1-90°_0-\tau_2-90°_0-$. Each excitation pulse lasted for 20 μs and was followed by a blanking period of 200 μs; during these times the detecting circuit was not connected to the coils, to avoid overload. In this particular test the single radiofrequency f_0 of the excitation pulses (5307 kHz) was slightly offset from one of the resonance frequencies $f_r = 5302$ kHz of ^{14}N nuclei in the sample, which was a sample quantity of the explosive HMX at a temperature close to 298 K. This produces a response showing variations at the beat frequency $f_0 - f_r$. The trace clearly shows the NQR echo responses occurring around the times $2\tau_1$, $\tau_2 + \tau_1$, $2\tau_2 - 2\tau_1$, and $2\tau_2$. A possible response at $2\tau_2 - \tau_1$ is either very weak or is thought perhaps not to exist at all. Parts 20 and 21 of the trace show the f.i.d.s after the first and third excitation pulses; the f.i.d. after the second pulse does not appear on this trace which shows the output of only one of two channels arranged to measure signals of opposite phase. The excitation signals in the second pulse may be in antiphase relationship with the signals of the first and third pulses.

From this trace it is clear that the three pulses generate at least four substantial echo response signals which in this instance are comparable with the largest measurable f.i.d. It will be noted that each of the echo responses is spread over a period of about 1 millisecond which is about twice the f.i.d. time constant T_2* and is fifty times longer than the excitation pulse length. The strength and duration of the echo responses are so great that by using them in addition to the f.i.d.'s the sensitivity of the tests can be greatly increased.

CLAIMS

1. A method of NQR testing which includes the steps of applying to a sample in which selected nuclei have an integral spin quantum number a series of at least three pulses of electromagnetic waves at a single radiofrequency to excite quadrupole resonance of the selected nuclei and detecting responses at a plurality of times when echo response signals are expected to occur.

2. A method as claimed in Claim 1 and wherein the responses to the excitation pulses are summed.

3. A method as claimed in Claim 1 or 2 and wherein the application and detection steps take place in the absence of an applied magnetic field.

4. A method as claimed in Claim 1, 2 or 3 and wherein the interval between the first and second pulses of the series is different from the interval between the second and third pulses.

5. A method as claimed in Claim 1, 2, 3 or 4 and wherein the pulses of the series are applied at times 0, τ_1 and τ_2 and the echo response signals are measured in periods embracing at least some of the times $2\tau_1$, $\tau_1 + \tau_2$, $2\tau_2$ and $2\tau_2 - 2\tau_1$.

6. A method as claimed in Claim 5 and wherein $\tau_2 > 2\tau_1$ and τ_1 and τ_2 have values which make the times τ_1, τ_2, $2\tau_1$, $\tau_1 + \tau_2$, $2\tau_2 - 2\tau_1$ and $2\tau_2$ separate and distinct from one another.

7. A method as claimed in Claim 5 or Claim 6 and wherein τ_1 is greater than one millisecond.

8. A method as claimed in any of the preceding claims and wherein the pulses of the series are applied at times τ_n, where n = 0 to N and N is greater than or equal to two, at least one of the pulses in the series being applied at a respective time $2\tau_n - \tau_{n-1}$ (n greater than one).

9. A method as claimed in any of Claims 5 to 7 and wherein a further pulse in the series is applied at time $2\tau_2 - \tau_1$ or $2\tau_n - \tau_{n-1}$ in general.

10. A method of NQR testing substantially as herein described with reference to the accompanying drawings.

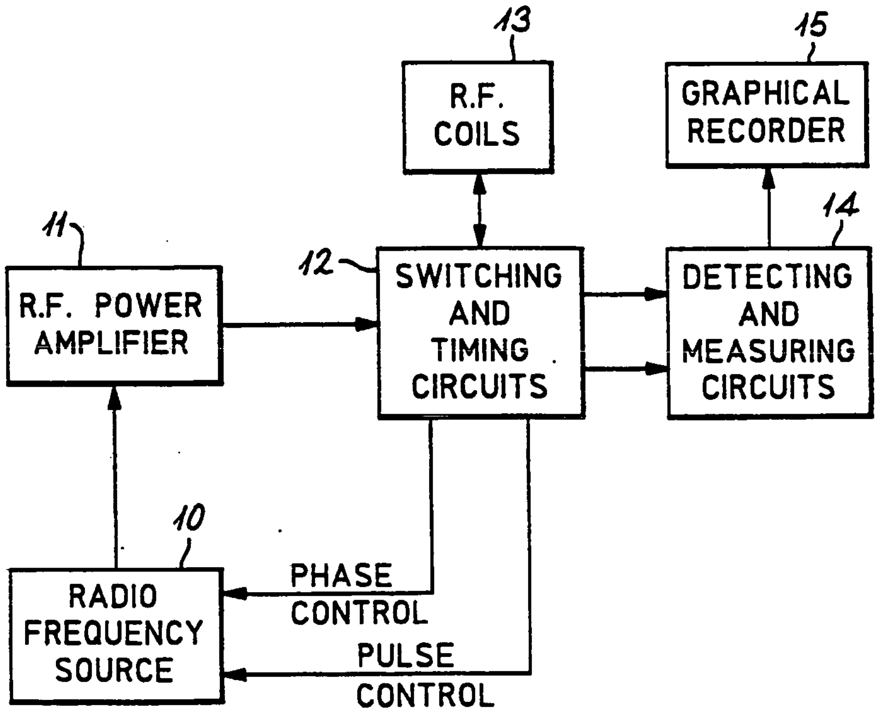
13
R.F.
COILS
15
GRAPHICAL
RECORDER
11
R.F. POWER
AMPLIFIER
12
SWITCHING
AND
TIMING
CIRCUITS
14
DETECTING
AND
MEASURING
CIRCUITS
10
RADIO
FREQUENCY
SOURCE
PHASE
CONTROL
PULSE
CONTROL

Fig. 1

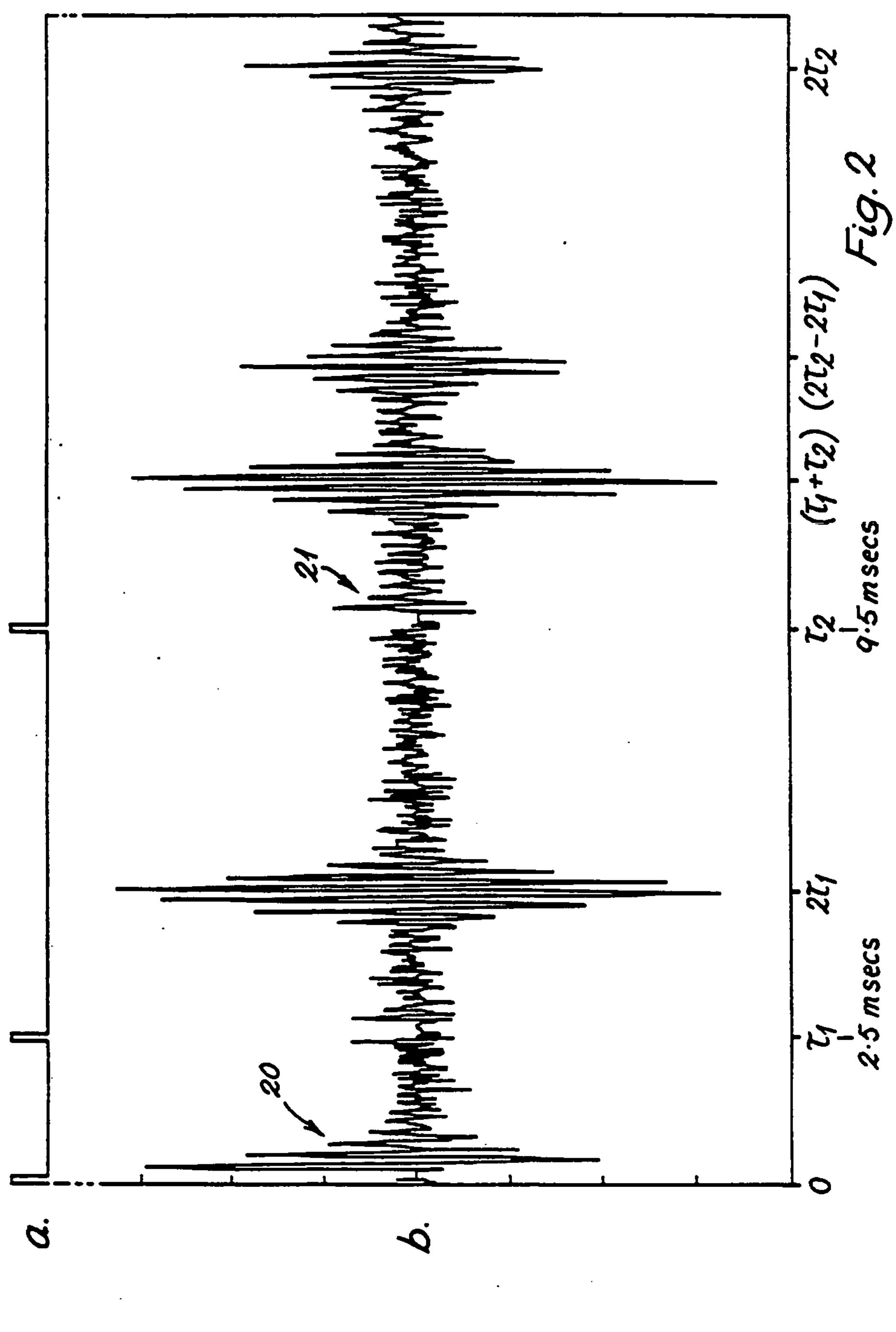
a.
b.
20
21
0
τ_1
2·5 msecs
$2\tau_1$
τ_2
9·5 msecs
$(\tau_1+\tau_2)$
$(2\tau_2-2\tau_1)$
$2\tau_2$

Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 92/02254

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 G01R33/44

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	G01R ; G01V ; G01N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category°	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	INSTRUMENTS AND EXPERIMENTAL TECHNIQUES. vol. 28, no. 2, 1 March 1985, NEW YORK US pages 426 - 428 A.A. BOGUSLAVSKII ET AL. 'AUTOMATIC NUCLEAR-QUADRUPOLE-RESONANCE MEASUREMENTS USING AN ELEKTRONIKA D3-28 MICROCOMPUTER' see the whole document ---	1-3
A	ELECTRO CONFERENCE RECORD vol. 4, 24 April 1979, LOS ANGELES US pages 1841 - 1845 J.R. GONANO 'NUCLEAR MAGNETIC RESONANCE AND NUCLEAR QUADRUPOLE RESONANCE FOR BOMB DETECTION' see the whole document ---	1-3

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
03 MARCH 1993	08 MAR 1993
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	HORAK G.I.

1

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	REVIEW OF SCIENTIFIC INSTRUMENTS. vol. 57, no. 3, 1 March 1986, NEW YORK US pages 393 - 403 A. BIELECKI ET AL. 'ZERO-FIELD NMR AND NQR SPECTROMETER' see the whole document ---	1-3
A	GB,A,2 200 462 (NATIONAL RESEARCH DEVELOPMENT CORPORATION) 3 August 1988 see abstract see page 3, line 6 - page 4, line 35 see page 5, line 21 - page 10, line 3 see page 12, line 33 - page 15, line 27; figures 1,2 ----	1-3

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 9202254
SA 67347

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 03/03/93
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2200462	03-08-88	EP-A- 0277745	10-08-88
		JP-A- 63259449	26-10-88
		US-A- 4887034	12-12-89

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